Aqueous Fuel Mixture

Internal combustion engines powered by combustible hydrocarbons cause system-related emissions in the form of nitrogen oxides, carbon monoxide and dioxide and particulates. Accordingly, the requirements which the emission levels of internal combustion engines are expected to satisfy have continuously increased in stringency in recent years. This applies not only to engines for motor vehicles of all kinds, but also to stationary units, for example the diesel engines used as generators or block power stations. In the Federal Republic of Germany, emission levels are regulated by the **"Technische Annleitung Luft (TA Luft)"** which stipulates NO_x limits of at most 2,000 mg/m^3 and limits for particulates of at most 130 mg/m^3 for stationary diesel units. These limits are to be lowered even further in the future, NO_x limits of 1,000 mg/m^3 and limits for particulates of 50 mg/m^3 being planned.

Accordingly, there is a considerable demand for emission-reducing measures in the affected industry. It has been known for some time that the addition of water to the fuel during its combustion considerably reduces NO_x, particulates and CO levels. However, water dissolves only sparingly in hydrocarbons. For example, only about 5% by weight of water dissolves in diesel oil, phase separation occurring with larger amounts. Accordingly, if relatively high percentages of water are to be formulated with hydrocarbons, suitable emulsifier systems have to be used. **DE-A 28 54 540** describes water-containing fuels comprising an emulsifier combination of alcohols and addition of products of ethylene oxide or propylene oxide onto C_{9-21} carboxylic acid amides. The emulsifiers are present in quantities of 0.5 to 26% by weight. C_{1-8} alcohols are disclosed as the alcohols. **DE 37 09 195 A1** describes storable water-containing fuel compositions which, besides hydrocarbons, contain a combination of 1.0 to 3.5% by weight of

an emuslifier and 0.5 to 10% by weight of C_{1-8} alcohols. **WO 85/04183** proposes water-based fuels containing 0.5 to 3.0% by weight of ethyoxylated C_{12-14} fatty alcohols as emulsifiers, the document in question failing to disclose the exact degree of ethoxylation.

However, the proposed water-containing fuels on the one hand are unable to satisfy the increased requirements the emission levels are expected to meet; on the other hand, the presence of emulsifiers can lead to engine problems, for example to the formation of deposits in and around the injectors or valves.

Accordingly, the problem addressed by the invention was to provide water-containing fuel systems that would not have any of the disadvantages mentioned above. It has been found that this problem can be solved by the choice of certain emulsifier systems.

BRIEF SUMMARY OF THE INVENTION

In a first embodiment, the present invention relates to a fuel mixture for internal combustion engines containing fuels, water and emulsifiers and optionally other additives, the emulsifier being a mixture of (A) branched-chain, saturated or unsaturated C_{12-24} fatty alcohols and (B) ethoxylated C_{8-24} fatty alcohols containing 1 to 10 mol ethylene oxide per mol fatty alcohol. It has surprisingly been found that this combination of emulsifiers enables fuels and water to be emulsified effectively and very quickly. The quantities of emulsifier used can be well below the known quantities. The fuel mixtures according to the invention preferably contain 60 to 95% by weight of the fuel, 5 to 35% by weight of water, 0.01 to 5% by weight of emulsifiers (A) and (B) and 0 to 2.5% by weight of other additives. Particularly preferred fuel mixtures contain 65 to 90% by weight of a fuel, 25 to 35% by weight of water, 0.01 to 0.5% by weight of emulsifiers (A) and (B) and 0.01 to 0.5% by weight of other additives.

Fuels in the context of the present invention are understood to be any energy-providing fuels of which the free combustion energy is converted into mechanical work. These include all kinds of motor and

aircraft fuels which ar liquid at room temperature and normal pressure. Motor fuels, for example for automobile or truck engines, generally contain hydrocarbons, for example gasoline or higher-boiling petroleum fractions. Diesel fuels are obtained from gas oil by cracking or from tars obtained in the low-temperature carbonization of lignitic or hard coal. Typical products have a density of 0.83 to 0.88 g/cm^3, a boiling point of 170 to 360°C and flash points of 70 to 100°C. In the context of the teaching of the present invention, diesel and heating oils are preferred fuels. In the water-fuel mixtures according to the invention, the water content - based on the mixture - is at least 5% by weight and at most 35% by weight. Aqueous mixtures containing about 70% by weight fuel and about 30% by weight water are particularly preferred. The emulsifier system described below is then added to these mixtures in the quantities indicated.

DETAILED DESCRIPTION OF THE INVENTION

Emulsifier components (A) and (B) are known classes of compounds. Fatty alcohols of component (A) are understood to be fatty alcohols corresponding to formula (I):

$$R^1OH \qquad (I)$$

in which R^1 is a branched hydrocarbon radical containing 12 to 24 carbon atoms and 0 and/or 1, 2 or 3 double bonds. Typical examples are isotridecyl, isohexadecyl, isostearyl or 2-hexyl-1-decane alcohol and 2-octyl decanol and technical mixtures thereof. Branched fatty alcohols of the type under discussion here may be obtained, for example, by standard methods, for example by oxo or Guerbet synthesis. The products of the Guerbet syntheses, which lead to alcohols all branched in the α-position, are preferred alcohols for the purposes of the present invention. Particularly preferred fuels contain branched, saturated C_{14-24} fatty alcohols as component (A).

The compounds of component (B) are also known compounds

obtained by reaction of C_{12-18} fatty alcohols with ethylene oxide under pressure in the presence of acidic or alkaline catalysts. Particulars of the process can be found in **"Surfactants in Consumer Products", Editor J. Falbe, Springer-Verlag, 1987, pages 87 to 93** and the literature cited therein. Suitable fatty alcohol ethoxylates contain 1 to 10 mol ethylene oxide units per mol fatty alcohol. C_{12-18} fatty alcohols containing 1 to 4 mol ethylene oxide per mol fatty alcohol are preferably used as starting products for the ethoxylation. Examples of suitable fatty alcohols are lauryl, myristyl, palmityl or stearyl alcohol. Suitable unsaturated fatty alcohols are, for example, oleyl alcohol and 10-undecen-1-ol. The fatty alcohol ethoxylates may also be present in the fuels according to the invention as mixtures of the various ethoxylates.

In another preferred embodiment, component (A) and component (B) are used in quantity ratios of 1:1 to 1:4. The total quantity of emulsifier components (A) and (B) used is preferably from 0.01 to 5% by weight, more preferably between 0.01 and 2% by weight and most preferably between 0.01 and 1% by weight, based on the quantity of fuel and water.

Besides the above-described emulsifiers (A) and (B), other nonionic emulsifiers known to the expert may be used in small quantities (i.e. about 5 to 10% by weight, based on the quantity of (A) and (B)). In general, however, there is no need for additional emulsifiers, i.e. fuels containing emulsifiers (A) and (B) only will be used.

Besides the emulsifiers (A) and (B), the fuels may contain other additives, preferably corrosion inhibitors, for example quaternized ammonium compounds or carboxylic acid amides and derivatives thereof. Particularly preferred corrosion inhibitors are ethoxylated carboxylic acid amides. Such amides correspond to general formula (II):

$$R^2\text{-CO-NX}R^3 \qquad \text{(II)}$$

in which R^2 is a saturated or unsaturated, linear or branched, optionally cyclic alkyl group containing 1 to 24 carbon atoms, X is a hydrogen atom or a methyl group or a group $-(C_2H_2-O)_n-H$ and R^3 is a group $-(C_2H_2-O)_n-H$ or a group $N-Y-(C_2H_2-O)_m-H$, where Y is a difunctional alkylene group containing 1 to 4 carbon atoms and n and m independently of one another have a value of 1 to 10. The compounds of formula (I) may be obtained by amidation of fatty acids or fatty acid mixtures and subsequent ethoxylation. Suitable fatty acids are octanoic, decanoic, lauric, myristic, palmitic, stearic, behenic, arachic, oleic, erucic, ricinoleic acid or mixtures thereof as found, for example, in coconut oil, palm oil, sunflower oil, safflower oil, soybean oil, castor oil, whale oil, fish oil or tallow. Preferred amides contain 12 to 24 carbon atoms and have been reacted with 0.5 to 5 mol ethylene oxide and preferably with 1 to 3 mol ethylene oxide per mol carboxylic acid amide. It is particularly preferred to use a tall oil fatty acid monoethanolamide containing 1.5 mol ethylene oxide per mol amide. In the production of these compounds, secondary products are formed in addition to the desired reaction products or educts, more particularly ethanolamine, triethanolamine or tall oil fatty acid, remain in the product. Technical mixtures such as these are also part of the disclosure of the present invention.

The emulsifier system according to the invention is added to the fuels in quantities of 0.01 to at most 5% by weight. A water-free additive concentrate containing components (A) and (B) and optionally other additives may advantageously be used for this purpose. Accordingly, the present invention also relates to water-free additive concentrates for water-containing fuels for internal combustion engines containing branched-chain, saturated or unsaturated C_{12-24} fatty alcohols, ethoxylated C_{8-24} fatty alcohols containing 1 to 10 mol ethylene oxide per mol fatty alcohol and ethoxylated carboxylic acid amides. The concentrates according to the invention contain emulsifier component (A) in quanities of 10 to 30% by

weight, mulsifier component (B) in quantities of 30 to 60% by weight and the ethoxylated carboxylic acid amides in quantities of 15 to 30% by weight.

The present invention also relates to a process for the production of water-containing fuels in which an additive concentrate as described above is added to the water-containing fuel, i.e. to the water/fuel mixture, in quantities of 0.01 to 5% by weight, preferably in quantities of 0.01 to 2% by weight and more particularly in quantities of 0.01 to 1% by weight.

Examples

An additive concentrate containing 20% by weight of 2-hexyl-1-decanol, 54% by weight of oleyl/cetyl alcohol x 2 EO and 26% by weight of tall oil fatty acid monoethanolamide x 1.5 EO was prepared and was then added to a mixture of 70% by weight diesel oil and 30% by weight water. The additive concentrate was used in a quantity of 0.1% by weight, based on the quantity of water and diesel oil. After brief stirring, a stable emulsion was formed and could be burned without difficulty in a diesel unit.

The fuel/water mixtures according to the invention are suitable as fuels for combustion engines of all kinds, but preferably for diesel engines, more particularly stationary diesel engines as used for block power stations. By using the fuels according to the invention, it is possible to reduce the emission of particulates and NO_x to below the present and future limits stipulated in "TA Luft" without any adverse effect on the combustion process or the engine. In addition, the fuel mixtures according to the invention are stable in storage, particularly at low temperatures, and may be obtained simply by mechanical mixing of the emulsifier system with the aqueous fuel.